KU LEUVEN

DIMAG - Electrically controlled ferromagnetism in 2-dimensional semiconductors

call: FLAG-ERA JTC2019

topic: 1. Synthesis and characterization of layered materials beyond graphene

start: 31 March 2020

Lino M.C. Pereira

Quantum Solid State Physics, KU Leuven, Belgium

on behalf of Michel Houssa (coordinator, KU Leuven) and the DIMAG consortium

the DIMAG consortium

	Country	Institution/ Department	Principal Investigators (PIs)
1 *Coord.*	Belgium	KU Leuven, Laboratory for Semiconductor Physics (**KUL1**)	**Michel Houssa**, Jean-Pierre Locquet
2	Belgium	KU Leuven, Institute for Nuclear and Radiation Physics (**KUL2**)	Lino M.C. Pereira
3	Germany	Hamburg University, Physics Department (**UHH**)	Michael Martins, Ivan Baev
4	France	Laboratoire de Physique des Solides, CNRS (**LPS**)	Antonio Tejeda, Vincent Jacques
5	Slovenia	University of Nova Gorica, Laboratory of Quantum Optics (**UNG**)	Giovanni De Ninno, Primož Rebernik, Barbara Ressel

the DIMAG project

Goal: new types of 2-dimensional ferromagnetic materials for spintronics

electrically controlled ferromagnetism, high spin polarization

fundamental research in nature, but aiming at device-compatible functionality

Model systems:

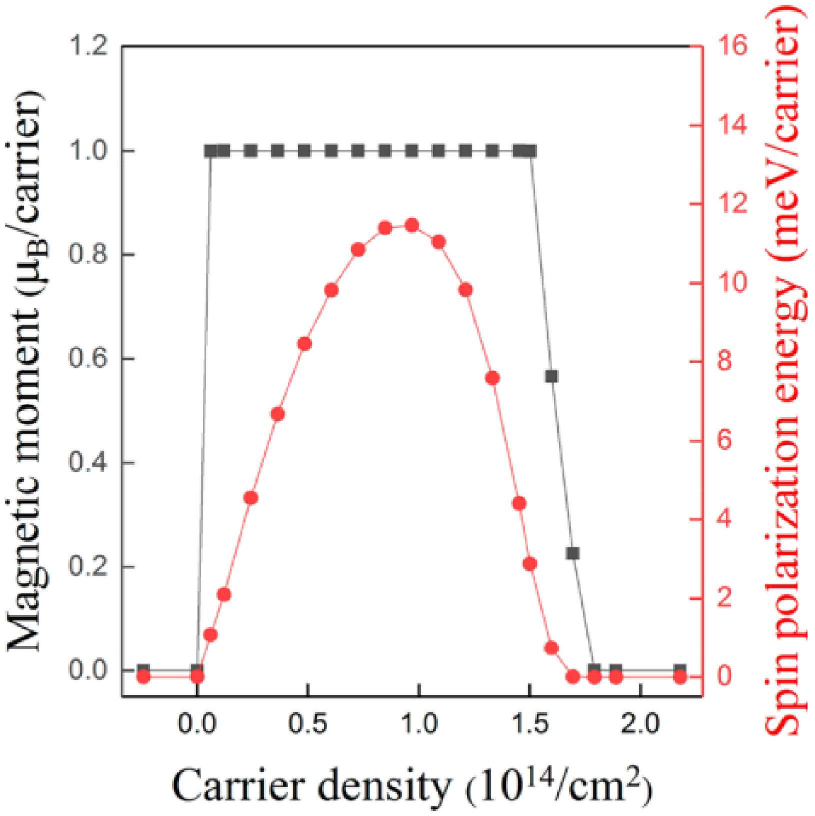
1) flat-band 2D semiconductors (InSe, …)
2) magnetically doped 2D semiconductors (Mn-doped MoS_2, …)
3) flat-bands in single-layer graphene (strain-induced pseudomagnetic field lattices)

the DIMAG approach

- theory (guide experimental work and to support data interpretation):
  density functional theory (DFT), molecular dynamics and Monte Carlo (KUL 1)
- growth/doping/modification of 2D materials by
  molecular beam epitaxy (MBE) and **ultralow energy ion implantation** (KUL 1,2)
- advanced studies of the electronic and magnetic properties using state-of-the-art techniques:
  - **scanning tunneling microscopy (STM) and spectroscopy (STS)**: probe structural, electronic and magnetic properties at the atomic scale (KUL 2)
  - **angle resolved photoemission spectroscopy (ARPES), and inverse photoemission spectroscopy (IPES)** (standard as well as spin-resolved and time-resolved): electronic structure (LPS, UNG)
  - **x-ray magnetic circular dichroism (XMCD):** spin and orbital magnetic momenta with element-specific capabilities (UHH, UNG)

system 1: flat-band 2D semiconductors

- 2D semiconductors (InSe [1], SnO [2],…) with flat bands
  - in the single-layer regime
- flat band → Van Hove singularity (VHS)
- VHS → Stoner-like ferromagnetism
  - in highly p-doped state
  - robust magnetization
  - high Curie temperature



half-metallic behaviour, with fully spin-polarized charge carriers

electrical control (acceptor doping and/or electrical gating)

[1] K. Iordanidou et al., *ACS Applied Nano Materials*. 2018; 1:6656
[2] [Houssa2018] M. Houssa et al., AIP Advances. 2018; 8:055010.

theory: hole-doping induced ferromagnetism in 2D materials

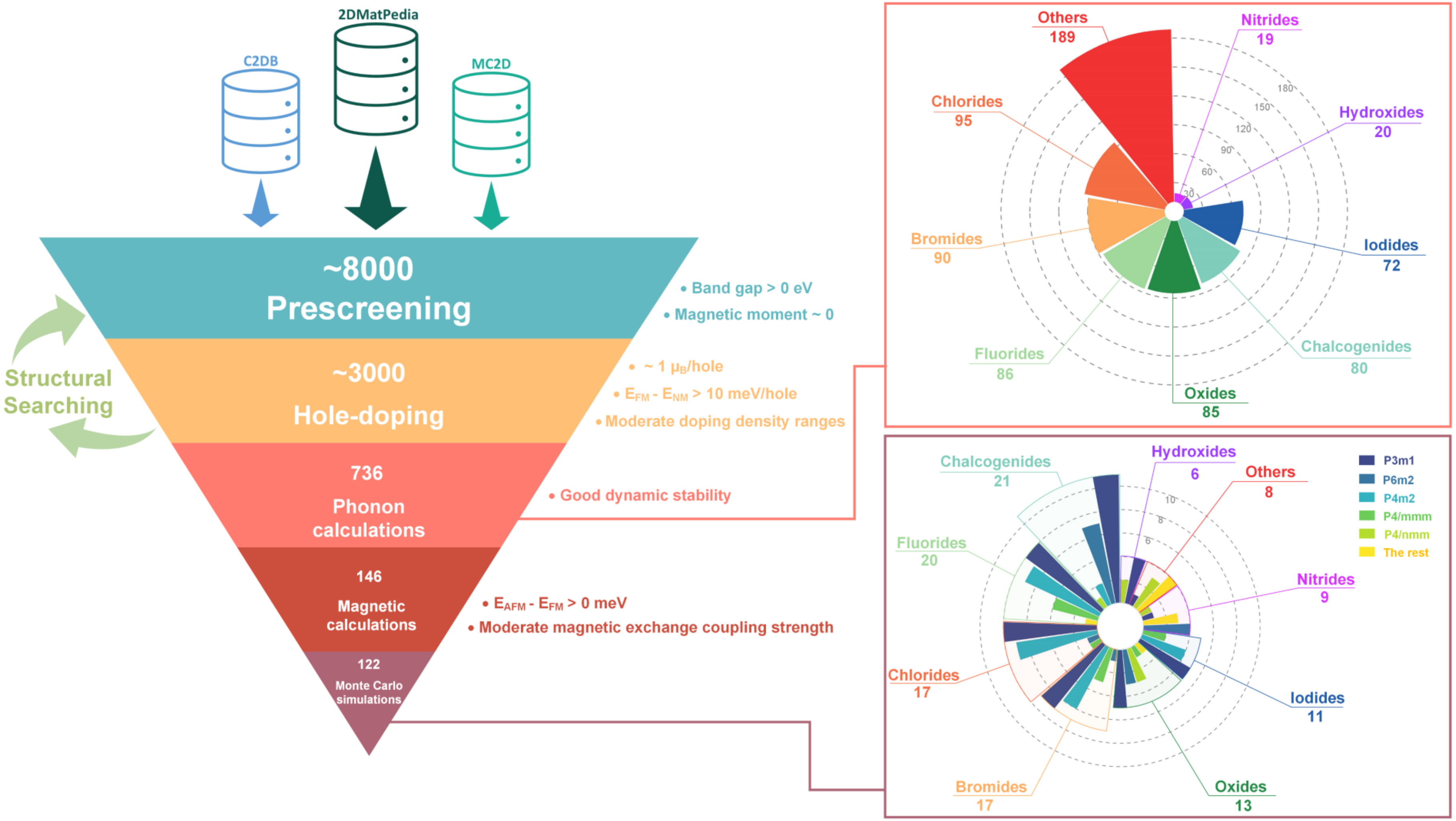
- DFT+MD+MC for screening compounds and crystal structures
  - evaluate structural/thermal stability
  - evaluate spin polarization, magnetic anisotropy and Curie temperature

[1] Meng *et al.*, "Two-dimensional gallium and indium oxides from global structure searching: Ferromagnetism and half-metallicity via hole doping", *J. Appl. Phys.* 128, 034304 (2020)

[2] Meng *et al.*, "Ferromagnetism and half-metallicity in two-dimensional MO (M=Ga, In) monolayers induced by hole doping", *Phys. Rev. Mater.* 4, 074001 (2020).

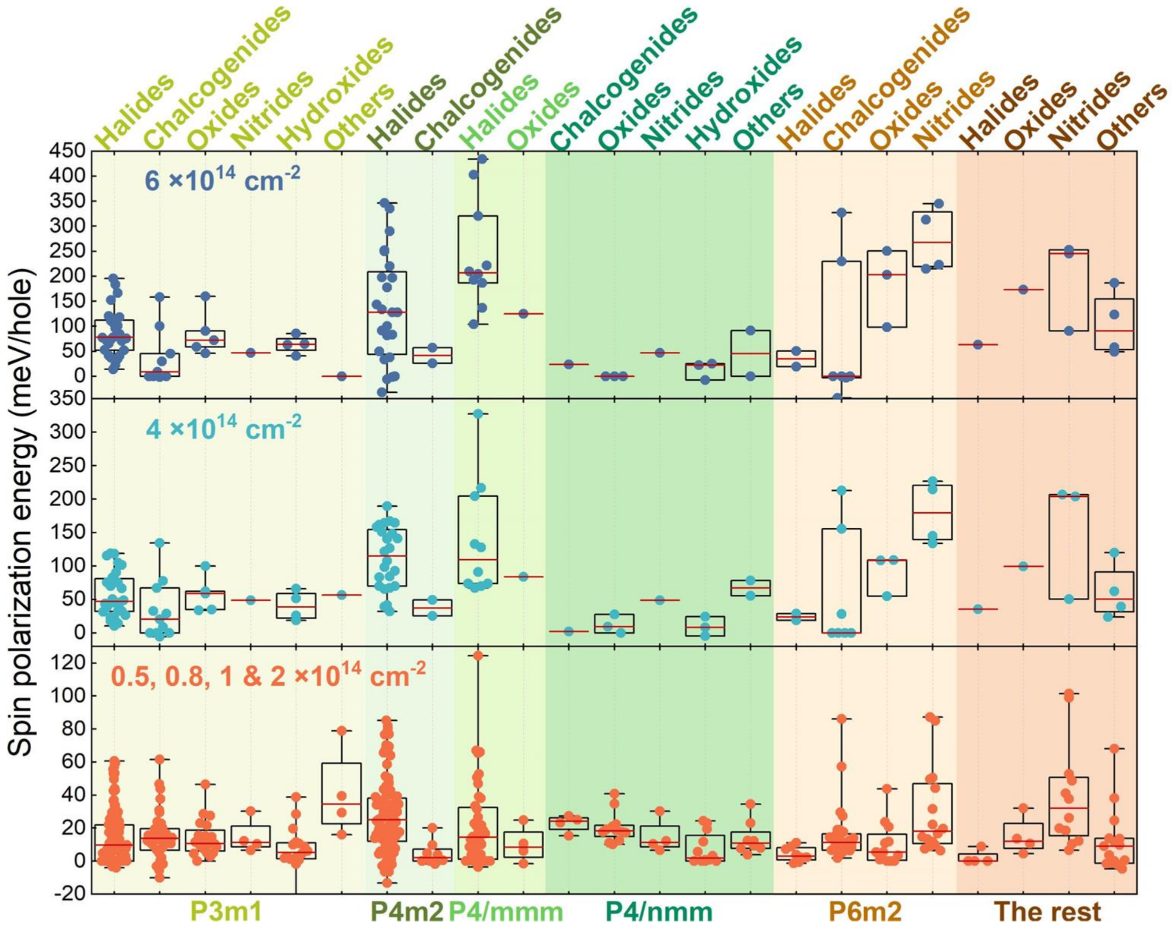
[3] Meng *et al.*, "Hole-doping induced ferromagnetism in 2D materials", *in preparation*.

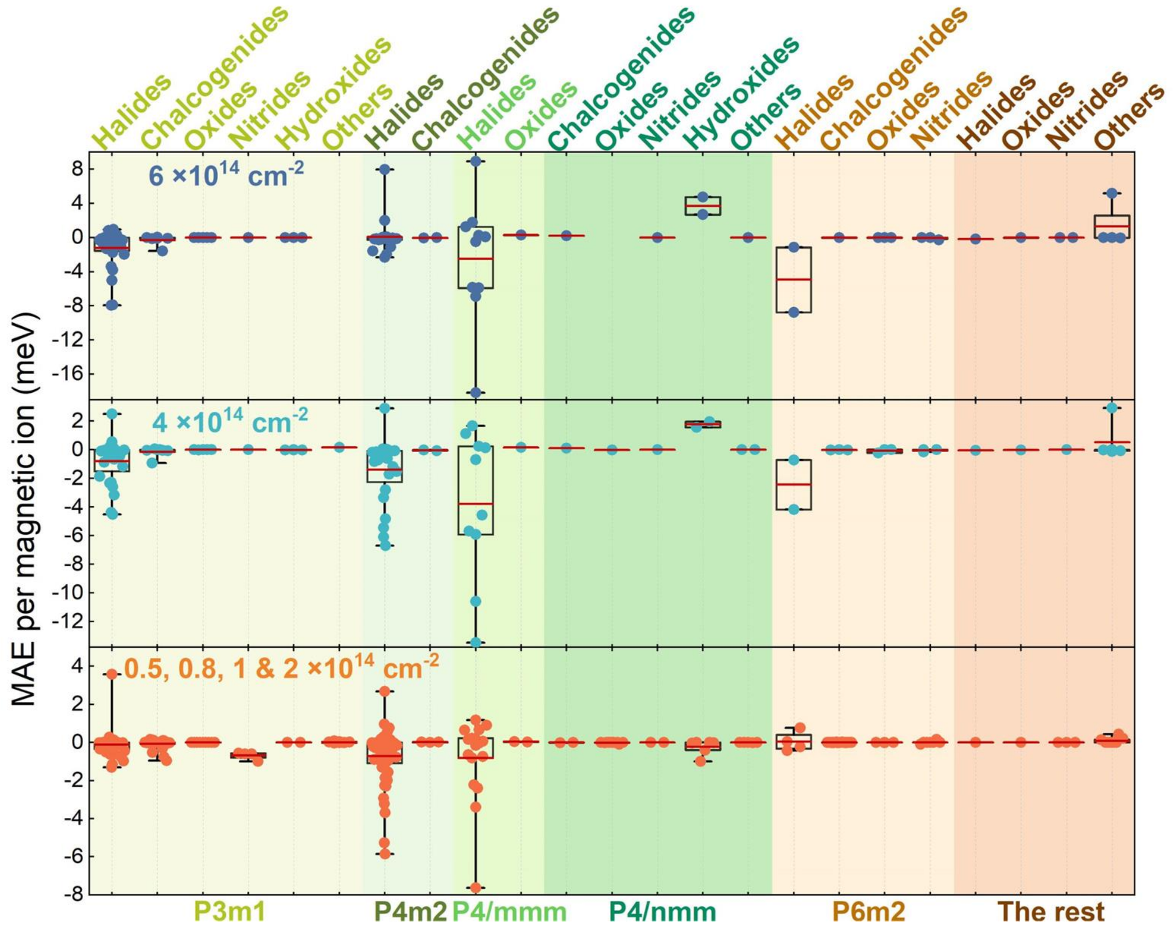
high-throughput first-principles simulations



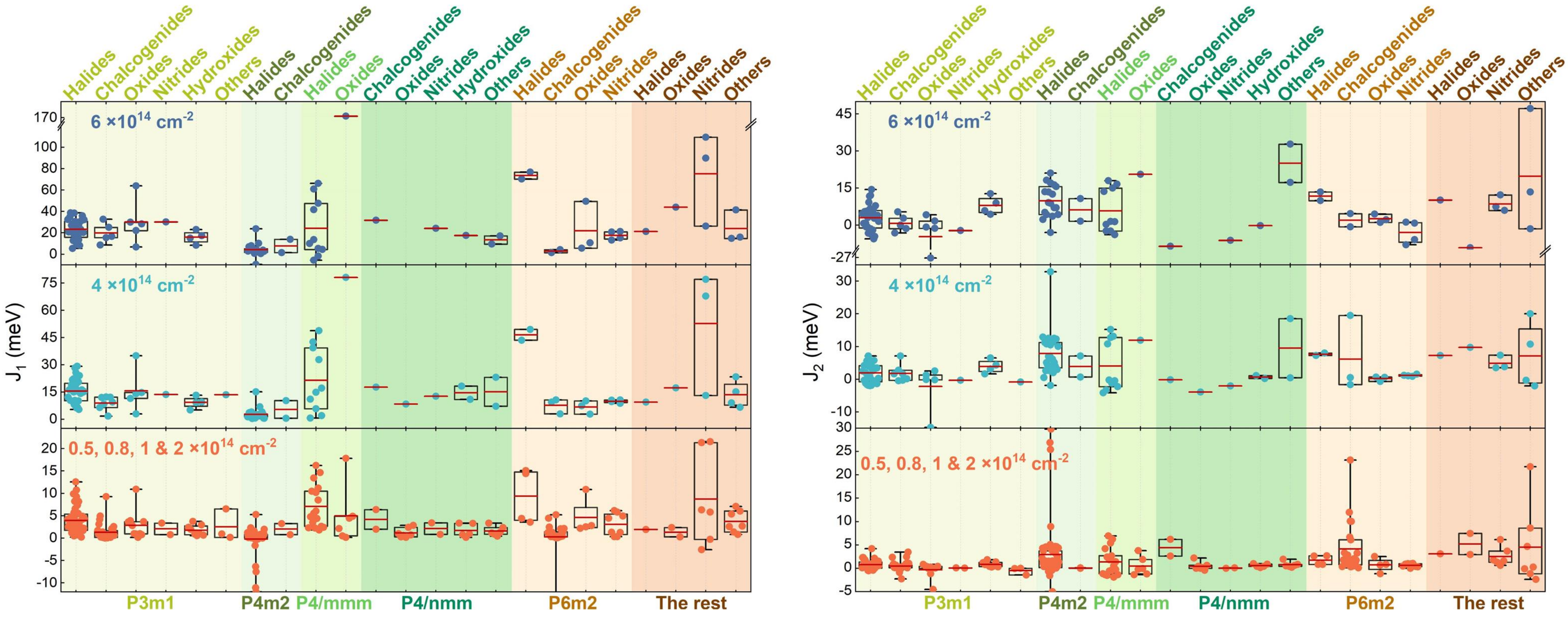
KU LEUVEN

high-throughput first-principles simulations

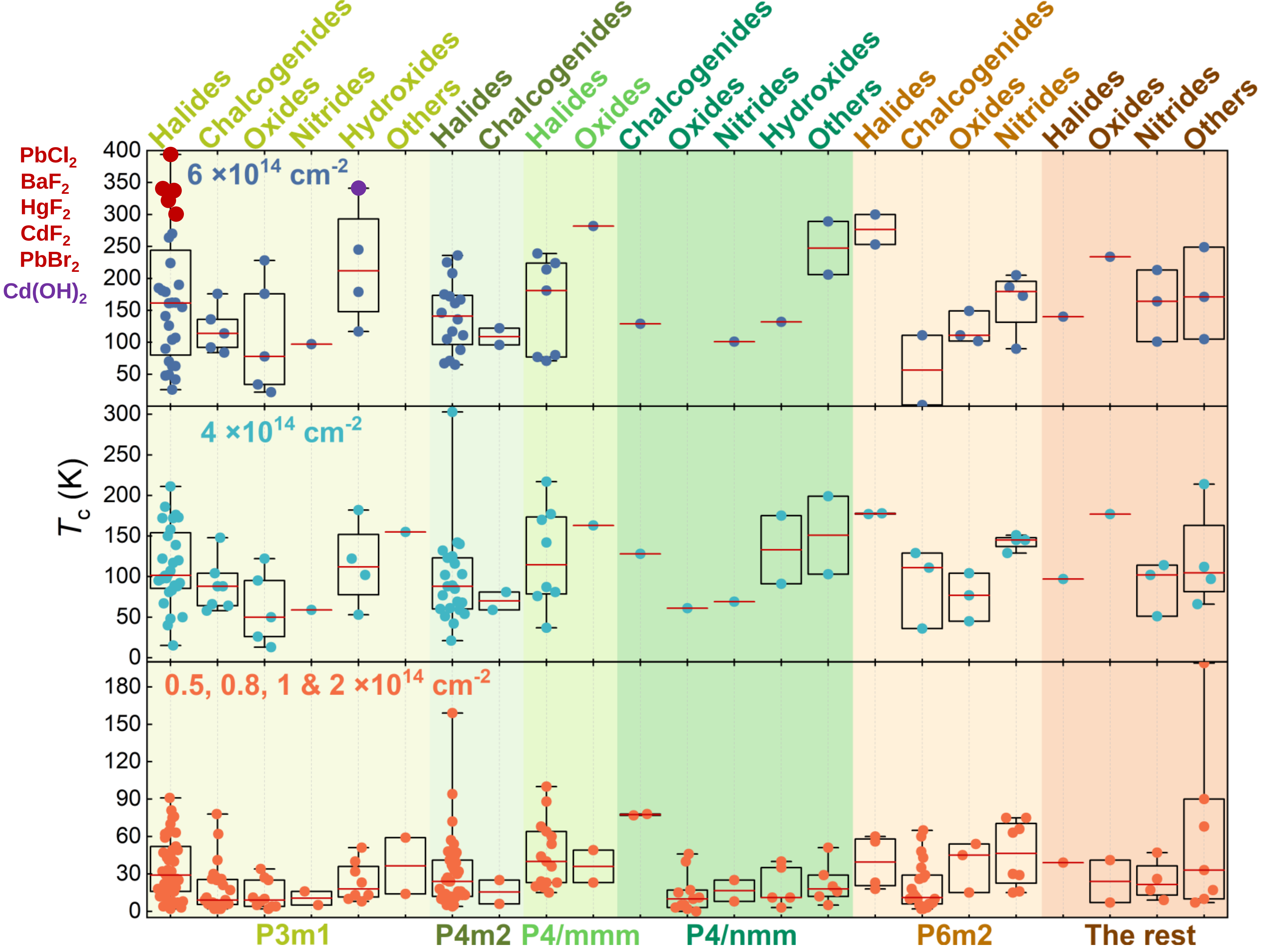




high-throughput first-principles simulations



KU LEUVEN



Halides
Chalcogenides
Oxides
Nitrides
Hydroxides
Others
Halides
Chalcogenides
Halides
Oxides
Chalcogenides
Oxides
Nitrides
Hydroxides
Others
Halides
Chalcogenides
Oxides
Nitrides
Halides
Oxides
Nitrides
Others
$PbCl_2$
BaF_2
HgF_2
CdF_2
$PbBr_2$
$Cd(OH)_2$
6 ×10^{14} cm^{-2}
4 ×10^{14} cm^{-2}
0.5, 0.8, 1 & 2 ×10^{14} cm^{-2}
T_c (K)
P3m1
P4m2
P4/mmm
P4/nmm
P6m2
The rest

system 1: flat-band 2D semiconductors

- metal halides take up the biggest proportion of the candidate materials, followed by the sulfides, oxides, etc.
- magnetic properties (spin polarization energy, magnetic anisotropic energy, magnetic exchange coupling parameters,…) generally improve with increasing hole doping density.
- Curie temperatures above room temperature are predicted for P3m1-$PbCl_2$ (394 K), $Cd(OH)_2$ (341 K), BaF_2 (337 K), HgF_2 (333 K), CdF_2 (320 K), $PbBr_2$ (301 K) and P6m2-$PbCl_2$ (300 K) and near room temperature for P4/mmm $Pb_2Br_2F_2$ (289 K) at a hole density of 6×10^{14} cm^{-2}.

we are currently developing the growth of single-layer InSe and GaSe

(lower T_C but exists in bulk)

challenge: few/single layer 2-dimensional growth

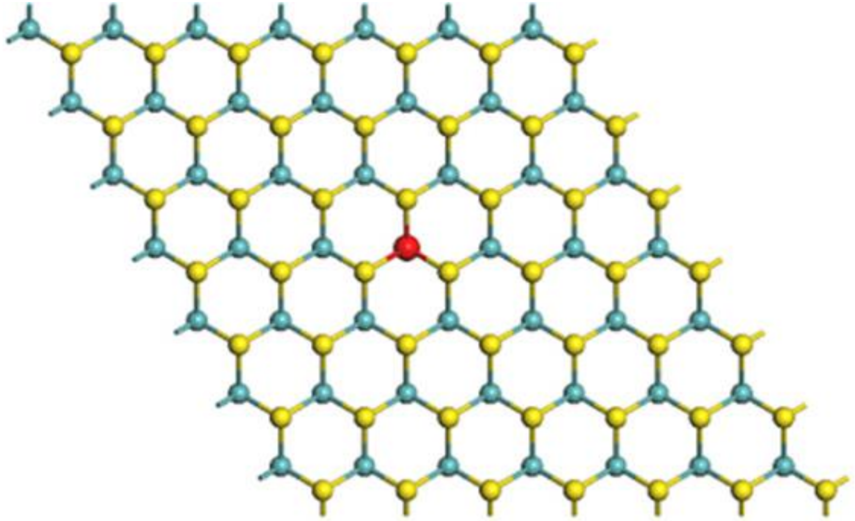
system 2: magnetically doped 2D semiconductors

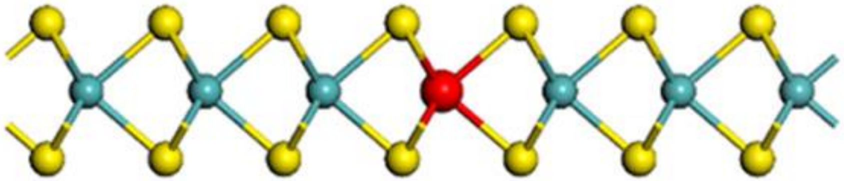
Growing reports of high temperature ferromagnetism in transition metal dichalcogenides (MoS_2, WSe_2) doped with transition metals

[Nat. Comm. 10, 1584 (2019),

Adv. Sci. 7, 1903076 (2020),

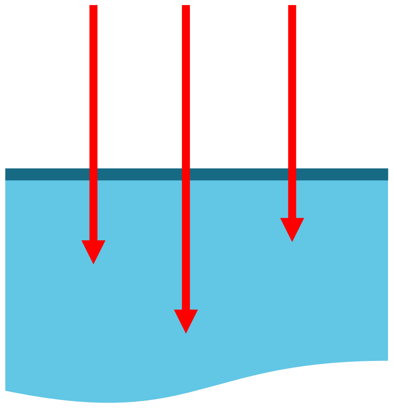
Phys. Rev. B 103, 094432 (2021), …]





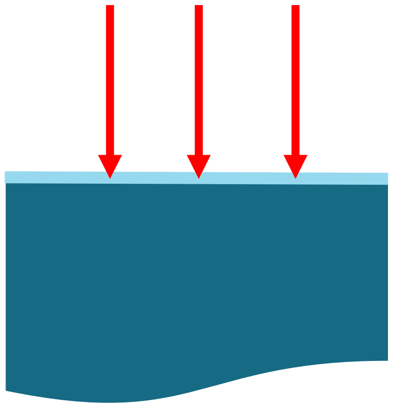
ultra-low energy (ULE) ion implantation

keV – MeV



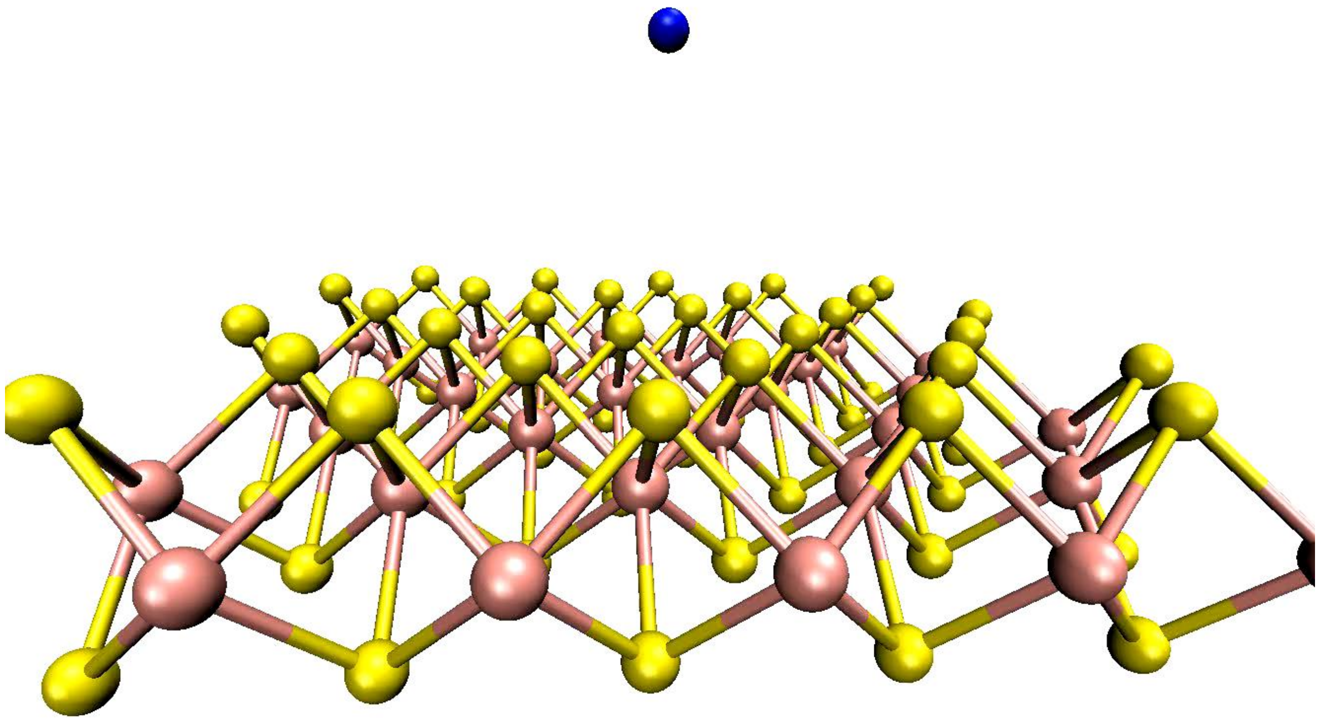
3D materials / bulk

~ 10-100 eV



2D materials / surface

ultra-low energy (ULE) ion implantation

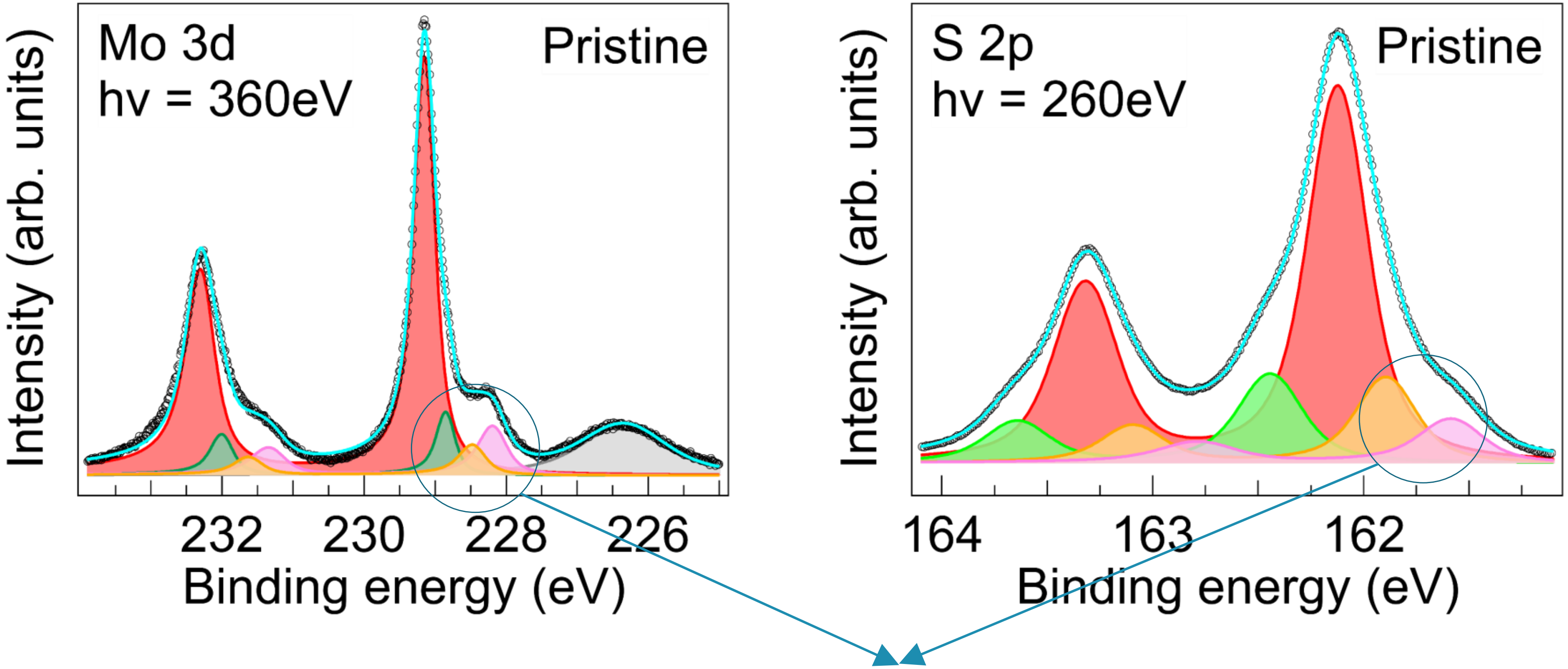


molecular dynamics + density functional theory

- any element of the periodic table
- control ion energy → incorporation
- beyond thermodynamically-favored incorporation configurations
- control number of implanted ions
- reproducible, scalable
- area-selective

system 2: magnetically doped 2D semiconductors

MoS_2/Au(111) grown by pulsed laser deposition



Pristine MoS_2 basal plane components

- Mo 3d at 229.25 eV and S 2p at 162.19 eV
- S in different environments: S top and S bottom

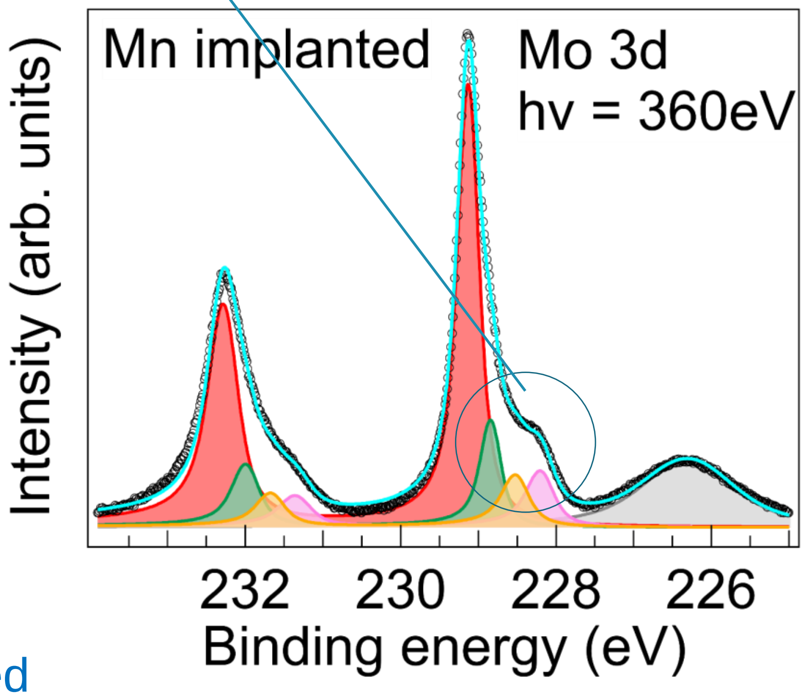
non-stoichiometric MoS_x ($1 \leq x \leq 2$) components

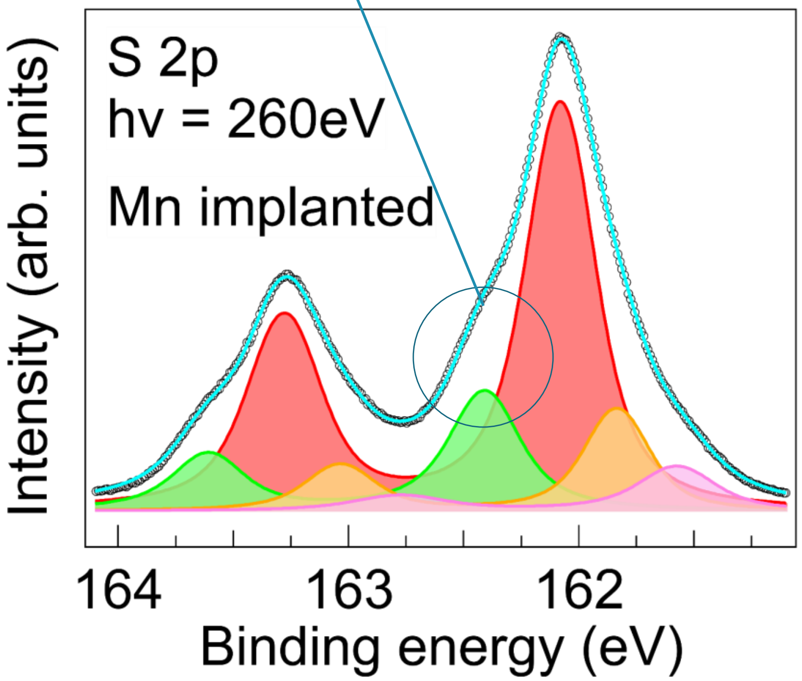
synchrotron x-ray photoelectron spectroscopy @SUPERESCA, ELETTRA

system 2: magnetically doped 2D semiconductors

MoS_2/Au(111) grown by pulsed laser deposition

increase in S deficient species, increase in S bottom peak compared to S top





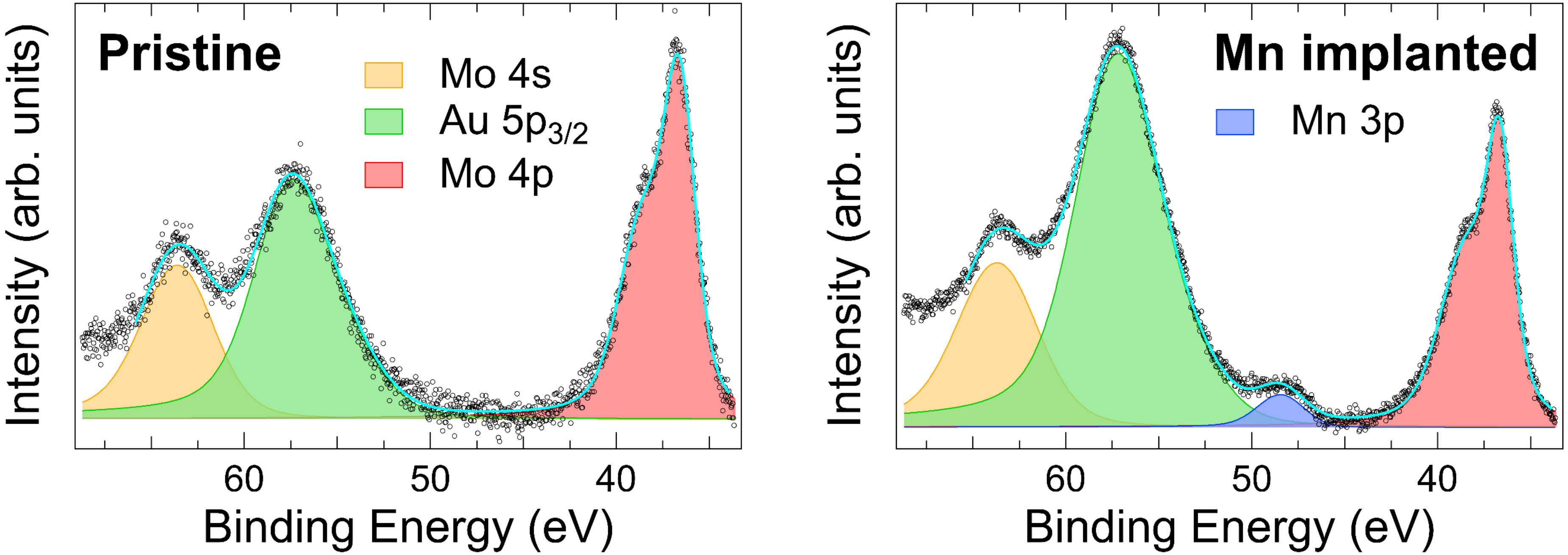
Mn-implanted

changes in core level spectra:

- Chemical signature retained
- Minimal increase in defect components

system 2: magnetically doped 2D semiconductors

MoS_2/Au(111) grown by pulsed laser deposition

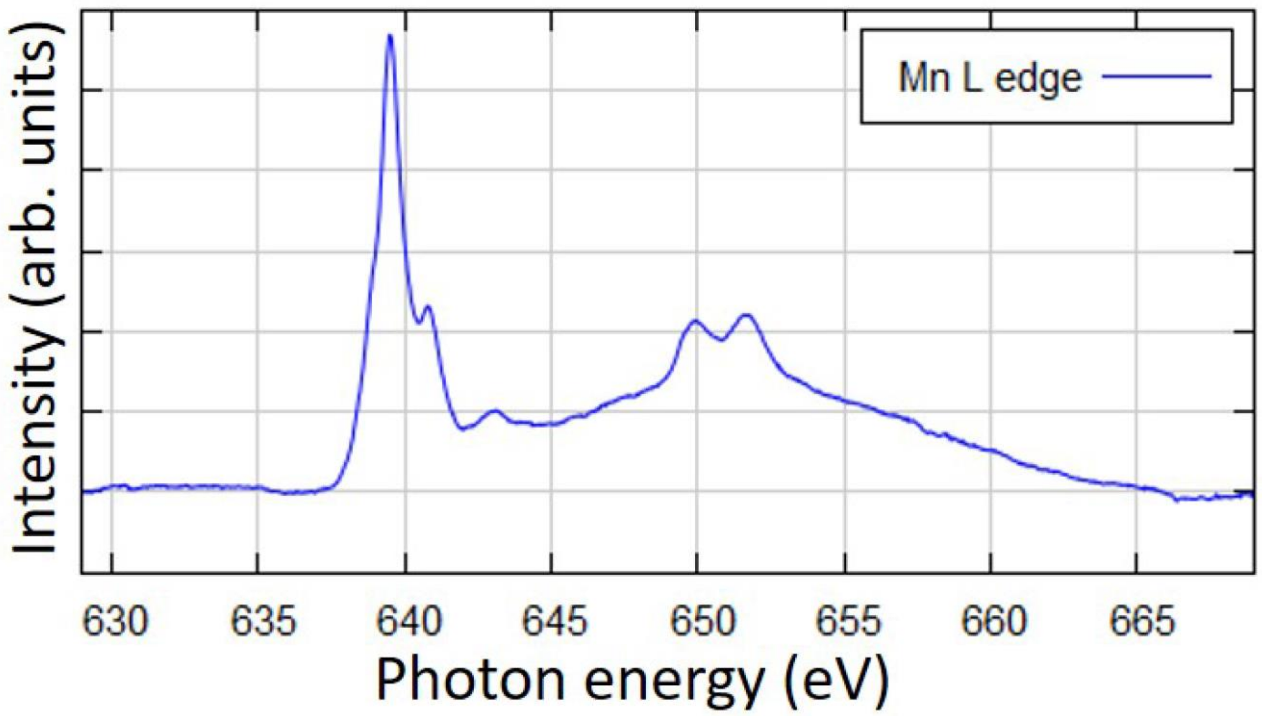


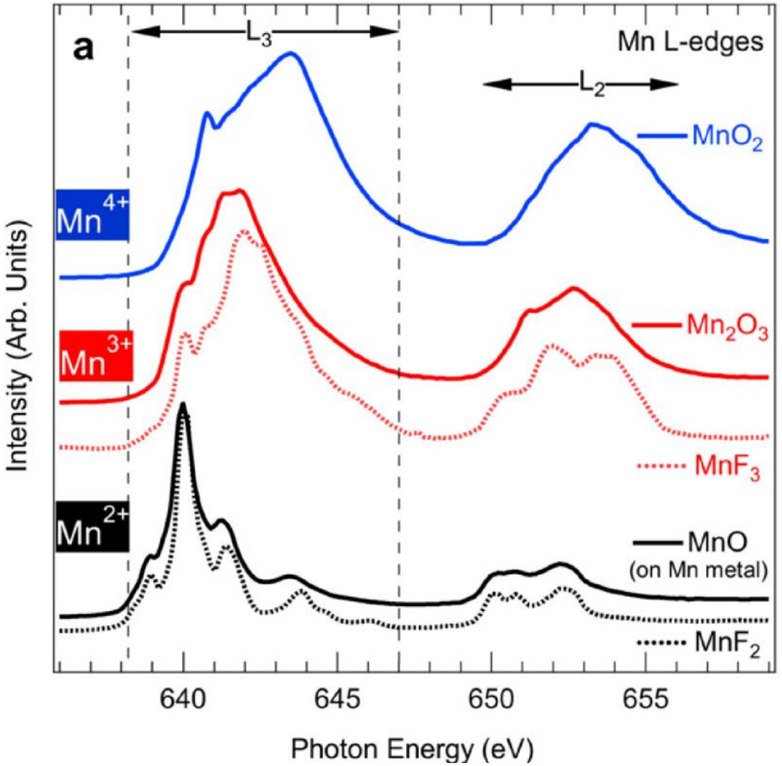
- relative **concentration of Mn: 4.4% monolayer equivalent**

  (MLE = surface atomic density of Mo in MoS2 on Au(111) i.e. 1.15 x 10^{15} atoms cm^{-2})

system 2: magnetically doped 2D semiconductors

MoS_2/Au(111) grown by pulsed laser deposition



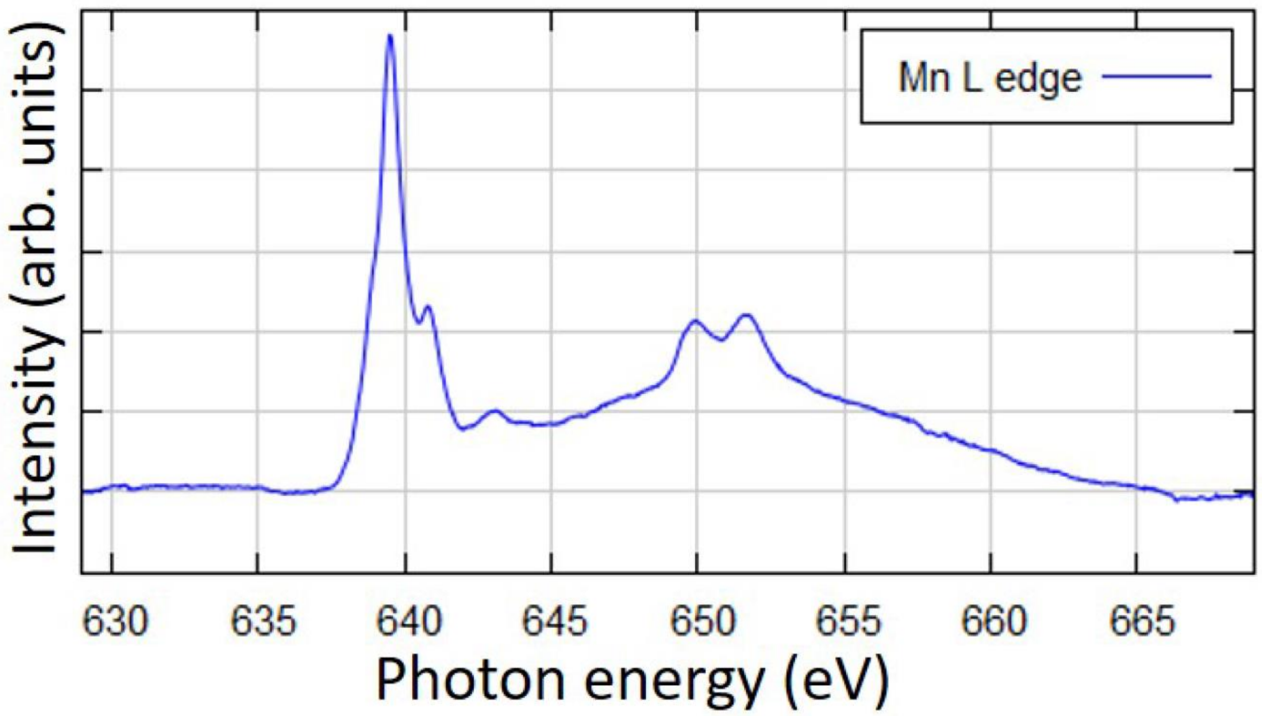


R. Qiao *et al.*, Current Applied Physics 13, 544 (2013)

- Mn L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) edges
- **low oxidation state: Mn^{2+} ($3d^5$)**

system 2: magnetically doped 2D semiconductors

MoS_2/Au(111) grown by pulsed laser deposition



however: X-ray magnetic circular dichroism measurements show vanishing Mn-related magnetization

↓

likely due to Kondo screening (metallic state induced by Au substrate)

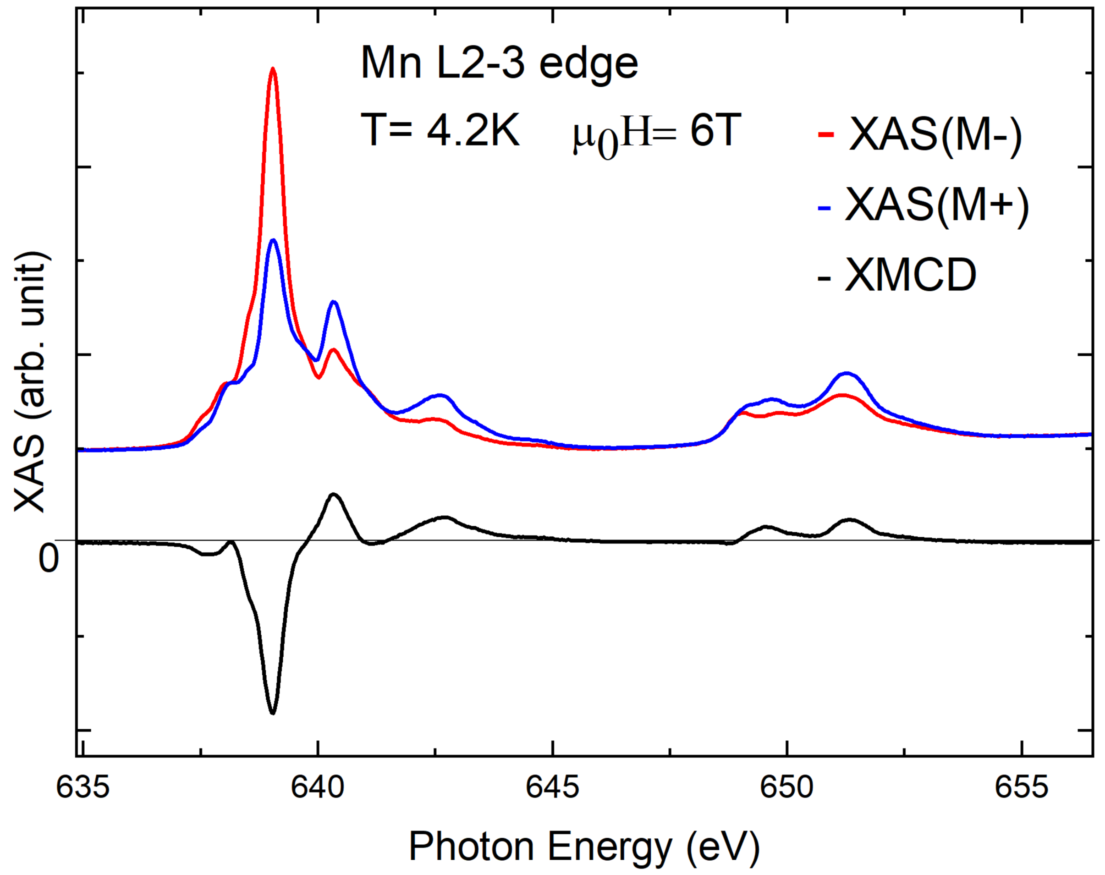
↓

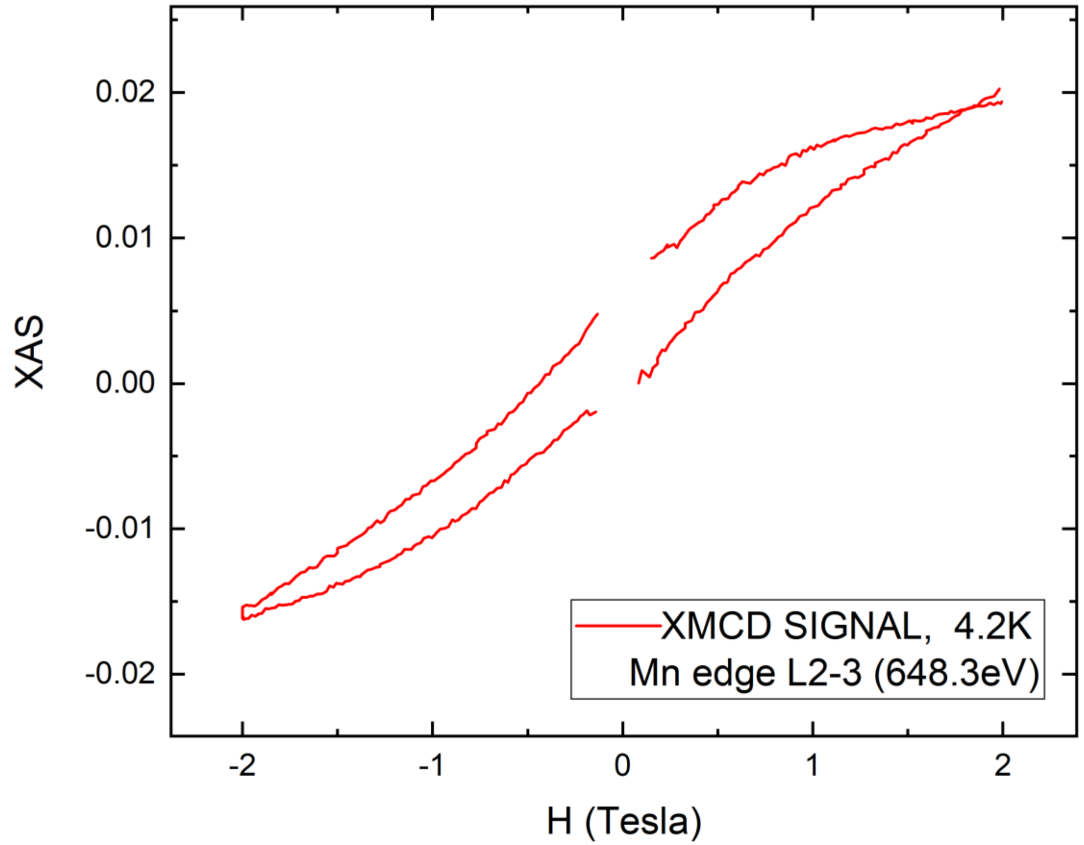
MoS_2/sapphire instead

- Mn L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) edges
- **low oxidation state: Mn^{2+} ($3d^5$)**

system 2: magnetically doped 2D semiconductors

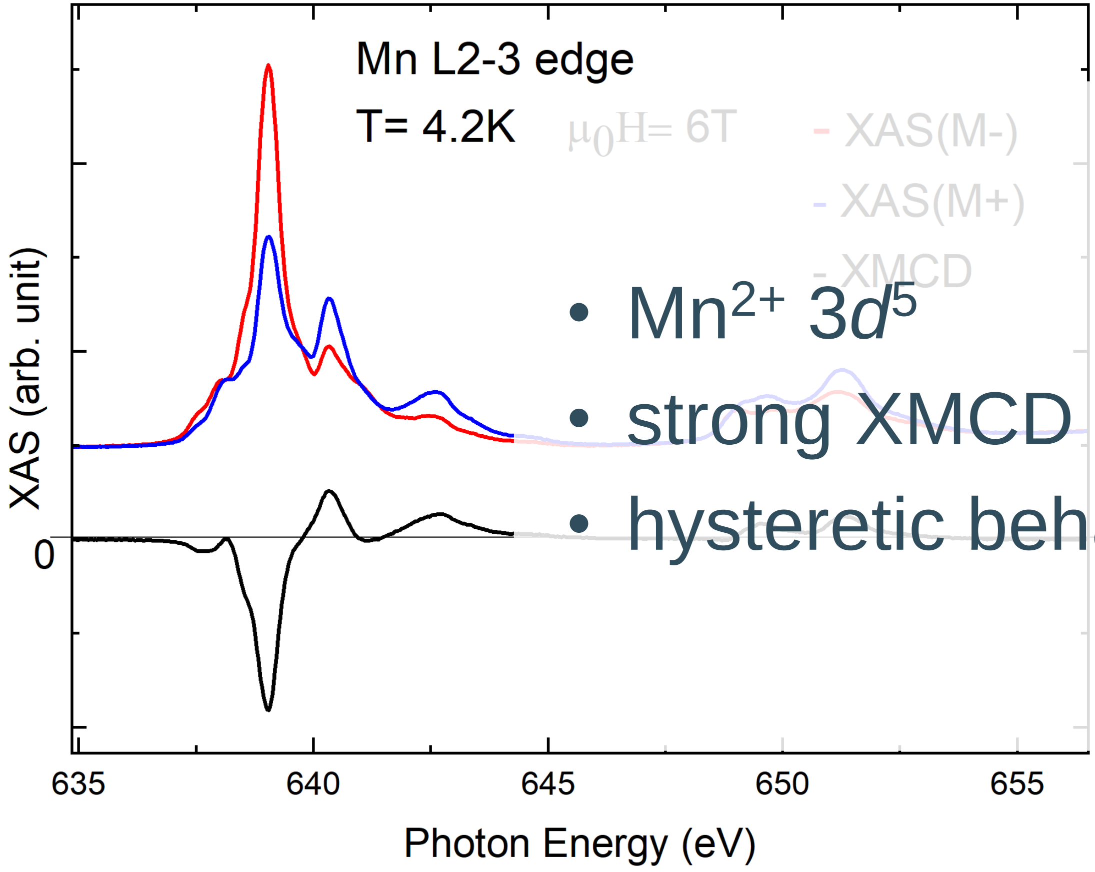
MoS_2/sapphire(0001) grown by chemical vapor deposition

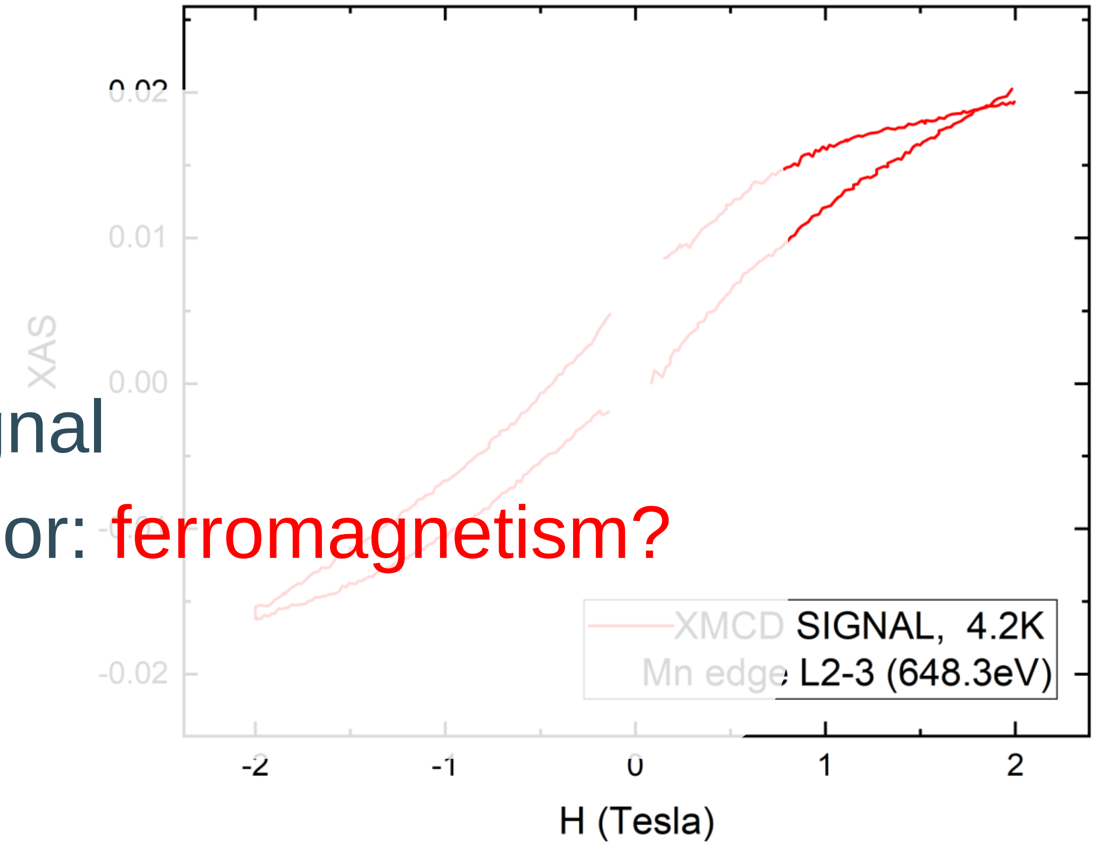




system 2: magnetically doped 2D semiconductors

MoS_2/sapphire(0001) grown by chemical vapor deposition

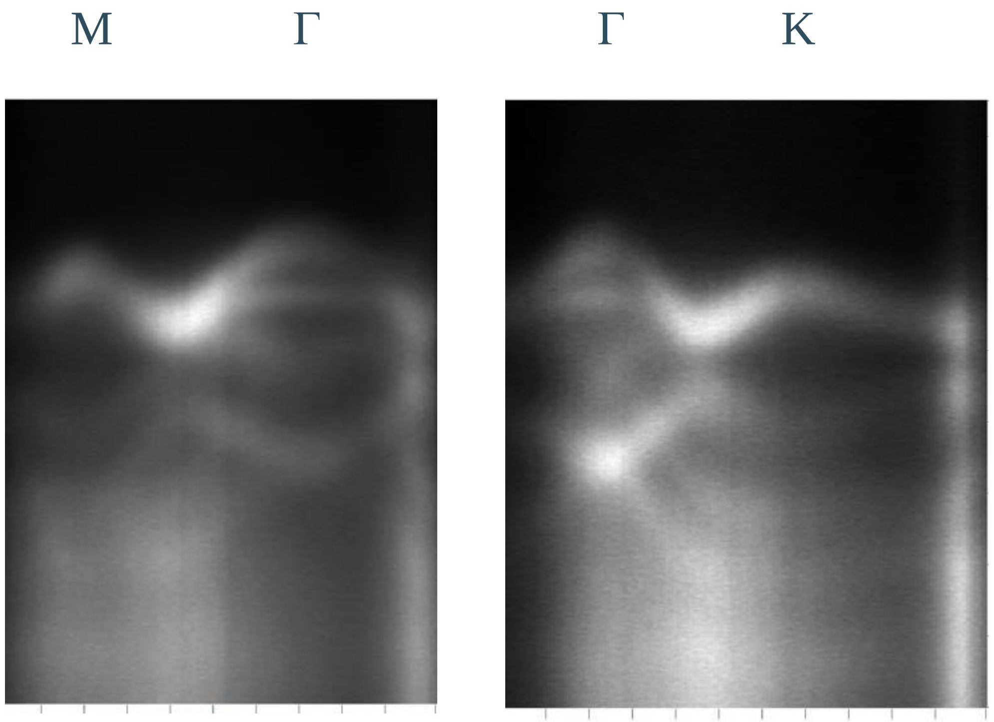




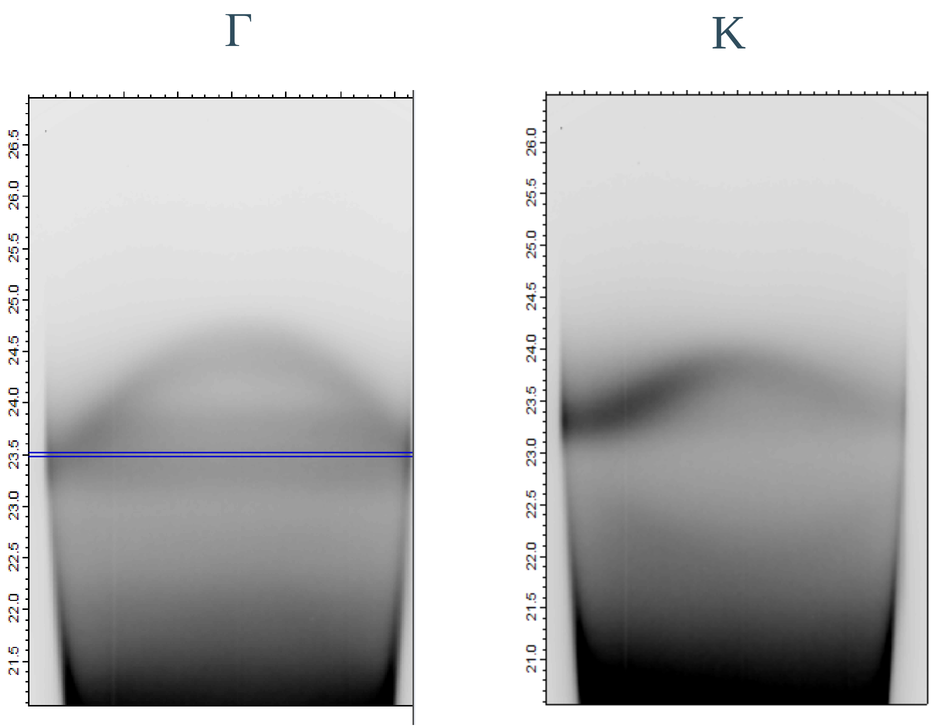
- Mn^{2+} $3d^5$
- strong XMCD signal
- hysteretic behavior: ferromagnetism?

system 2: magnetically doped 2D semiconductors

MoS_2/sapphire(0001) grown by chemical vapor deposition



ARPES

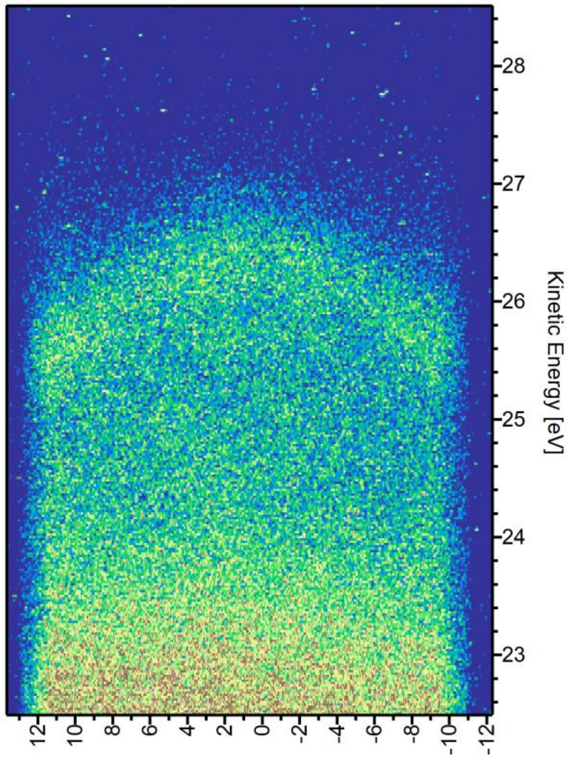


synchrotron ARPES
@ BaDElPh, ELETTRA

system 2: magnetically doped 2D semiconductors

MoS_2/sapphire(0001) grown by chemical vapor deposition

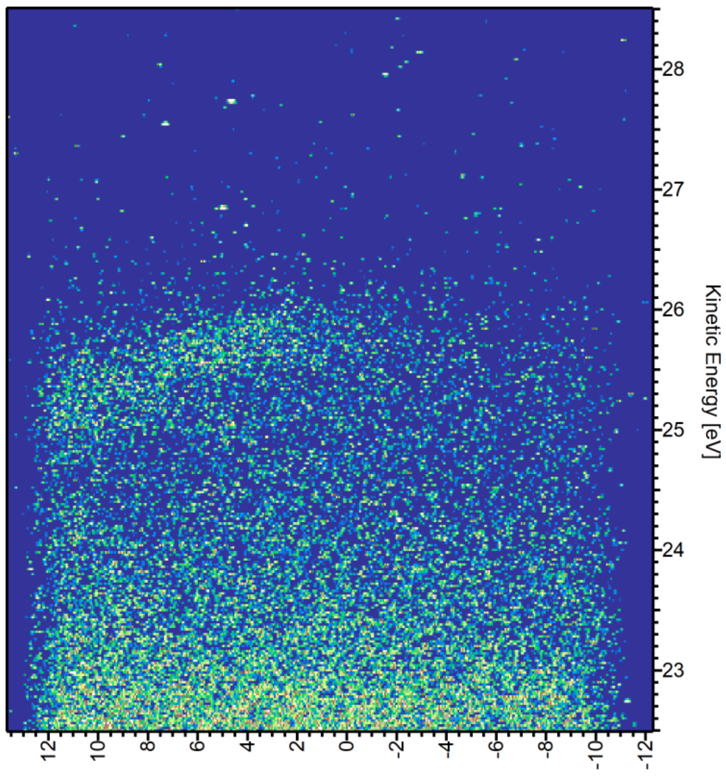
Γ



pump-probe time-resolved ARPES (UNG)

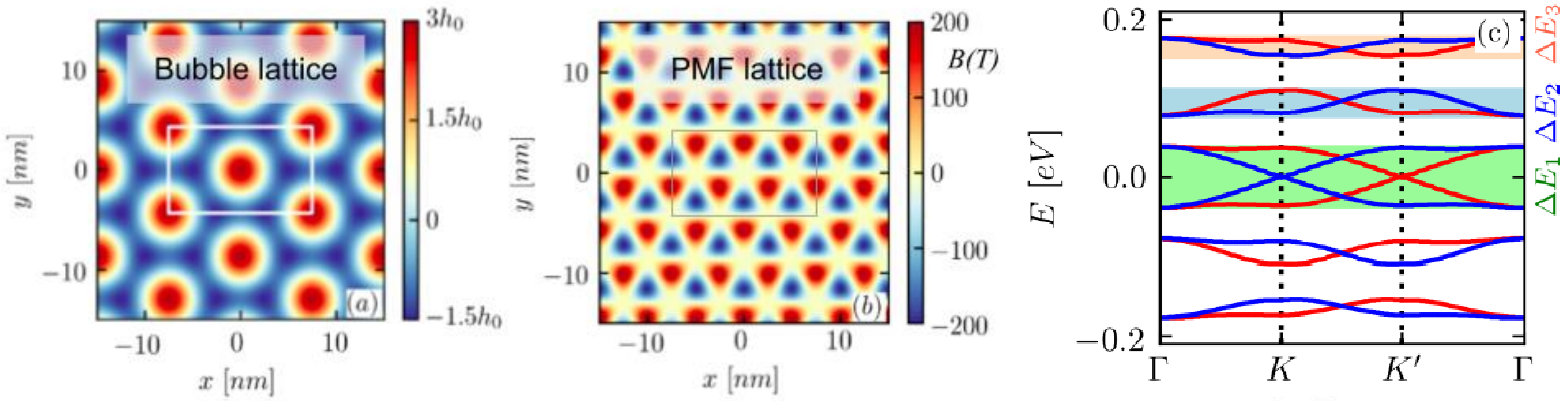
(so far) unable to observe conduction band

K



system 3: flat-bands in single-layer graphene

periodic, strain-induced pseudomagnetic fields



system 3: flat-bands in single-layer graphene

periodic, strain-induced pseudomagnetic fields